ABSOLUTE AQUEOUS REDOX POTENTIALS

(*via* a new link between aqueous and gaseous properties)

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on the occasion of the 3 main anniversaries,

1) **90th**: foundation of Masaryk Univ. (MUNI),
2) **90th**: foundation of Mendel Univ. of Agriculture & Forestry (MUAF),
3) **50th**: award of the Nobel Prize in 1959 to Professor J. Heyrovský,

and also 3 more anniversaries,

4) **70th**: survival of MUNI & MUAF in 1939,
5) **40th**: survival of MUNI & MUAF again in 1969 and
6) **20th**: " velvet revolution" in 1989.

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1. INTRODUCTION

" Chemistry is electric" (Bk: M.E. Bowden, CHF, 1997)

Tomato and Lemon batteries:
http://www.funsci.com/fun3_en/electro/electro.htm http://www.youtube.com/watch?v=AY9qcDCFeVI

Electrolyte: acidic juice, Electrodes: copper (+) and zinc (-).
Chemical reactions at the two half cells: (1) Cu^{++} + 2e- ==> Cu and (2) Zn ==> Zn^{++} + 2 e- ; the overall reaction is Zn + Cu^{++} ==> Zn^{++} + Cu.
The cell voltage is the " potential difference" between the two half cells.

Electrochemists have chosen by convention, the potential of the standard hydrogen electrode (S.H.E.) as zero. The redox reaction for this half cell is $2H^+ + 2e^- <==> H_2$. The standard potentials, E^o(S.H.E.) of Cu and Zn are +0.34 and -0.76 V and the cell voltage is, E = +0.34 - (-0.76) = +1.10 V.
(*Note*: The unit of potential is named volt, in honor of Volta)

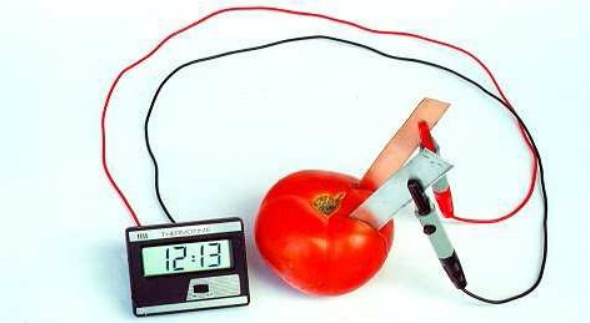

Figure 15 - LCD-Clock powered by a tomato battery.

1. INTRODUCTION (contd.)

Latest news on S.H.E. : " ..universal reference electrode for which, under standard conditions, the standard electrode potential (H^+/H_2) is zero at all temperatures: Last update: 2009-06-16; http://goldbook.iupac.org/S05917.html

There have been attempts in the past to obtain the absolute value of the potential of the S.H.E. (Bard et al [1]). Trasatti (1986) [2] suggested, by theoretical calculations, the value 4.44 (+/-) 0.04V.

Recently, Donald et al (2008) [3] obtained for S.H.E. (by electron capture on gaseous phase nano-drops) the value, 4.20 (+/-) 0.4 V.

The " new observation here" that E^o varies linearly with the ionization potentials (I) for many groups of elements, has given the " absolute potential of the S.H.E., ($E^o_{I=0}$)" (which confirms the value in [3]) (and can be taken as the *final answer*).

Thereby, the " absolute redox potentials, have been obtained as the sum, $E^o_{abs} = E^o + E^o_{I=0}$" , (Heyrovska, [4]).

2. LINEAR DEPENDENCE OF AQ. STD. POTENTIALS (E^o) ON IONIZATION POTENTIALS (I)

The data in [1] have been used to plot E^o *vs* I in Fig. 1, where I = I (sum) is the sum of the 1st, 2nd, .. ionization potentials, as the case may be, depending on the value of n, (ox + ne^- = red).

$E^o = k_{aq}I - E^o_{I=0}$; absolute aq. redox potential = $E^o_{abs} = E^o + E^o_{I=0}$

$E^o_{I=0}$ = Abs. potl. of S.H.E. = 2.87 V (H^-/H: halogens) & 4.20 V (H^+/H: all others)

(Author: Raji Heyrovska, Brno Conference, 29-30 June 2009)

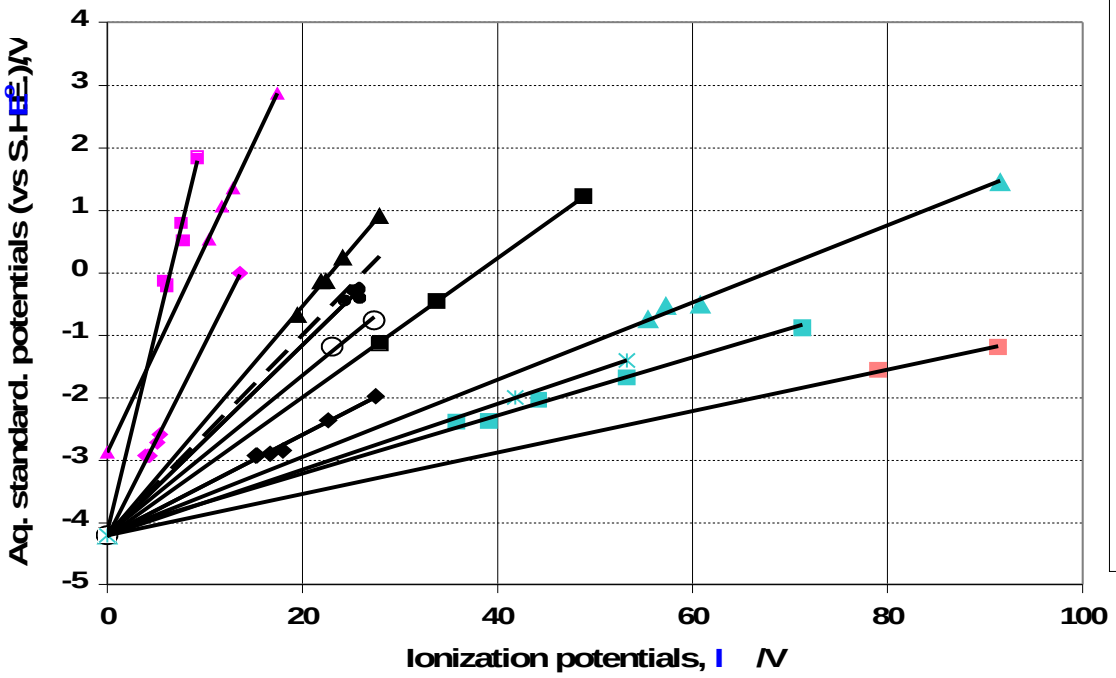

Fig. 2. Linear dependence of aq. std. potls. on I.

All the straight lines in Fig. 1 follow the simple equation,

$$E^o = k_{aq} I - E^o_{I=0} \; ; \; E^o_{abs} = E^o + E^o_{I=0} \; (= k_{aq} I) \qquad (1a,b)$$

where k_{aq} is the slope, " $E^o_{I=0}$ is the absolute potential of the S.H.E." and " E^o_{abs} is the absolute redox potential" . $E^o_{abs} = E^o_{I=0}$ when $E^o = 0$ (Eq. 1b).

For Gp. VIIA (halogens, $(1/2)X_2/X^-$), $E^o_{I=0} = 2.87$ (+/-) 0.01 V, and for the others, $E^o_{I=0} = 4.20$ (+/-) 0.03 V, which correspond to the $(1/2)H_2/H^-$ and H^+/H redox equilibria resply. Fig. 2 shows plots of E^o_{abs} $(= k_{aq} I)$ *vs* E^o.

The slopes (k_{aq}) of the lines have been used as criteria for classifying the redox couples into groups (i) to (xii) (see: the box in Fig. 1).

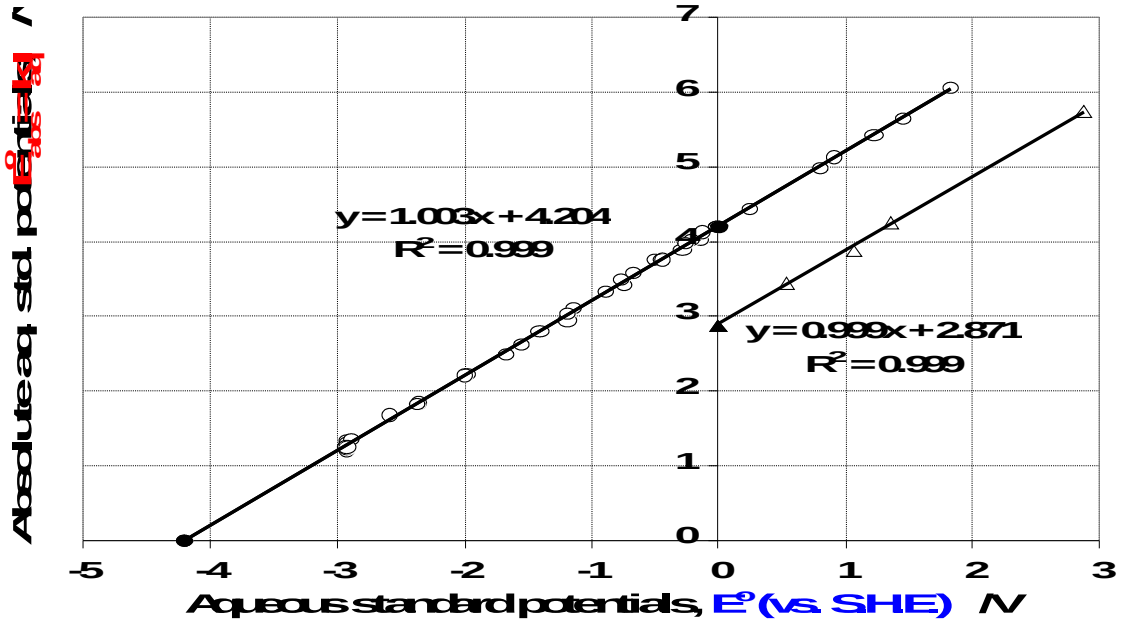

Fig. 2: Absolute aq. std. potentials, E^o_{abs} (calculated as $k_{aq} I$) *vs* E^o.

3. DEPENDENCE OF POLAROGRAPHIC HALF-WAVE POTENTIALS ($E_{1/2}$) ON IONIZATION POTENTIALS (I)

Fig. 3 shows the $E_{1/2}$ values for Cu, Pb, Cd, Zn, Mn, Ba (n = 2 for all) Al (n = 3) (Heyrovsky, Ilkovic [5a,b]) and Tl (n = 1) (Heyrovsky, Kuta [6]). The causes for the differences between E^o and $E_{1/2}$ in some cases (here, Ba and Al) have been explained by Lingane [7].

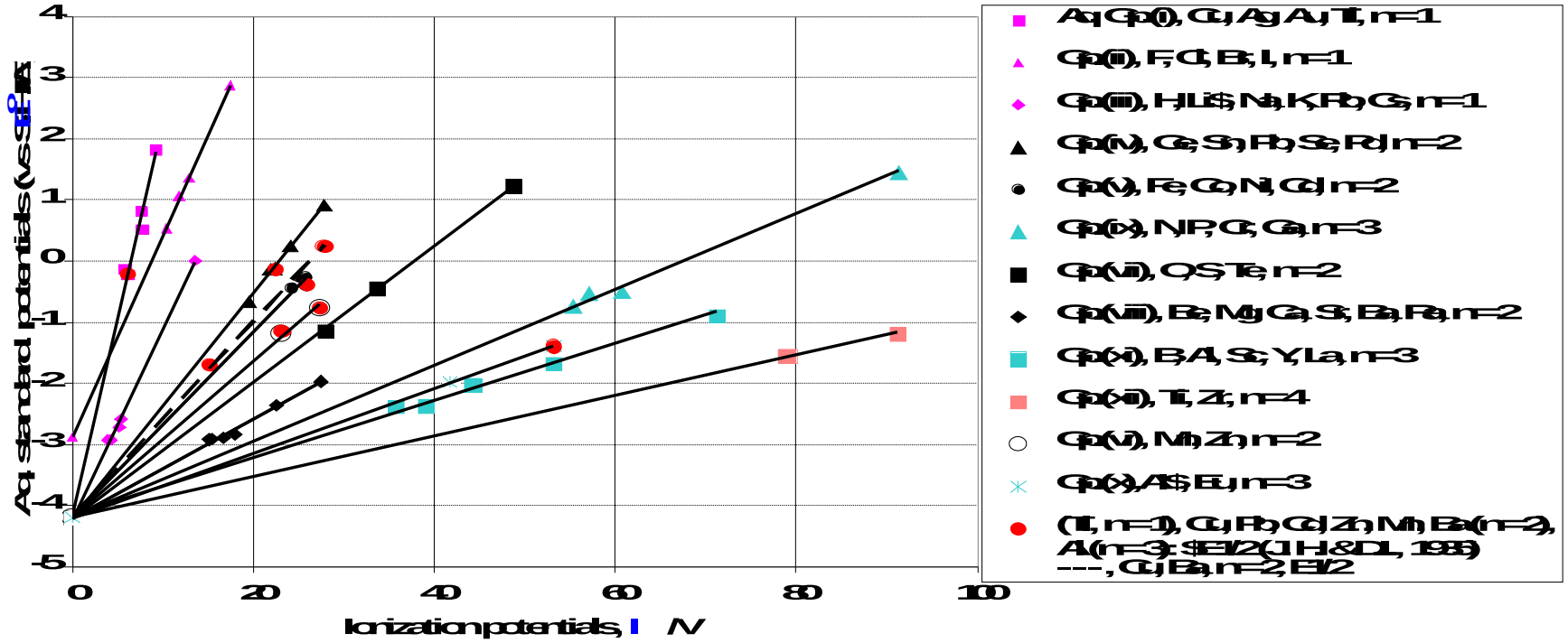

Fig. 3 Linear dependence of E^o on I.
Red filled circles: $E_{1/2}$ values

ACKNOWLEDGEMENTS

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